THE EFFECT OF CATALYSTS ON COAL GASIFICATION

Reuel Shinnar
C.A. Feng
Alan I. Avidan

Department of Chemical Engineering
The City College of the
City University of New York
New York, New York 10031

INTRODUCTION

There have been a number of studies dealing with the impact of various catalysts in coal gasification (1,2,3,4,5) and one catalytic process for SNG (6) has been operated successfully in a large pilot plant. This paper analyzes the potential value of catalysts in coal gasification. The paper will first discuss what is the proper operating range for a gasifier by reviewing the thermodynamic and kinetic constraints of coal gasifiers, then analyze the question as to what type of catalyst is really required. Both syngas processes and SNG production will be discussed.

There are a few separate areas in which catalysts would be valuable in coal gasification.

1) <u>SNG Production</u>. In SNG production it has already been shown (8) that there would be a significant process advantage for a catalyst that could operate at 1000-1100°F. The global equilibrium at these temperatures contains mainly CH_4 and CO_2. The reaction heat requirements are low and can be supplied by superheated steam, which simplifies the process considerably. Steam conversion is low, but this disadvantage is overcome by the other advantages of such a simple process. The lowest operating temperature that has been achieved with good conversion of carbon and steam is 1300°F. Operating at 1300° requires a very high concentration of potassium hydroxide or potassium carbonate in the coal. As recovery is difficult, the high concentration of potassium increases catalyst losses and reduces the economic incentive. At a temperature of 1300°F significant amounts of CO and H_2 are formed. The process developed by Exxon separates these gases from the methane and recycles them to the reactor. This requires a catalyst with a high methanation activity. We will show that a catalyst operating at 1400-1500° could also be acceptable but the process would have to be modified. By proper modification this process should be competitive with the process proposed by Exxon and could utilize cheaper catalysts, or lower catalyst concentrations.

2) <u>Syngas Generation</u>. In syngas generation the thermodynamic optimum (8) is at conditions where coal gasification is fast. However, for many coals it is difficult to operate at these conditions. The only gasifier that has achieved operation close to the thermodynamic optimum is the British Gas Corporation slagging-type gasifier or BGC slagger. However, the BGC slagger is not suitable for all coals. In fluid bed gasifiers, one has to operate at lower temperatures to prevent agglomeration or ash melting. Under such conditions high conversion of the char is difficult as the gasification reaction is very slow at temperatures below 1700°F if char conversion is to exceed 70% (9).

The Winkler gasifier as well as present second generation fluid bed gasifiers for syngas all operate in a partial oxidation regime which reduces their thermal efficiency and increases the amount of oxygen required. A proper catalyst operating at 1500-1600°F could allow high

carbon and steam conversion and could potentially solve the inherent operating problems faced by all fluid bed gasifiers.

3) Gas Cleanup. The third area in which catalysts could significantly contribute to improved coal gasification processes is in the area of gas cleanup. There is a strong advantage in devolatilizing the coal prior to feeding it to the gasifier. However, this leads to the formation of tars and phenols which require expensive gas cleanup, and prevent efficient heat recovery from the product gas. If those products could be cracked at high temperatures, preferably in the devolatilization zone itself to methane and char, this would simplify the process scheme.

4) Improved Devolatilization. In a two-stage process, the results obtained in the devolatilization zone are very important. The amount of coal devolatilized in this stage as well as the product distribution strongly depends on the devolatilization conditions. A proper catalyst could change both the product yield and product distribution in the devolatilizaton zone.

Aside from the development of the Exxon process, most work on the effect of catalysts has concentrated on item two: acceleration of the gasification reaction. Almost no measurements are available as to whether these catalysts also accelerate the methane formation reaction, nor is there any reported study of the effect of catalysts on items 3 and 4 listed above.

Let us now shortly discuss each item separately.

1) Use of Catalysts in SNG Production

The thermodynamic and kinetic constraints of SNG processes are discussed in detail in (ref. 10), and we will here only summarize them.
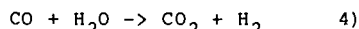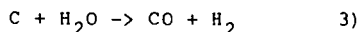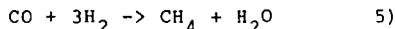
Present catalysts do not promote the direct reactions

$$C + H_2O \rightarrow 1/2CH_4 + 1/2CO_2 \qquad\qquad 1)$$

$$1.5C + H_2O \rightarrow 1/2CH_4 + CO \qquad\qquad 2)$$
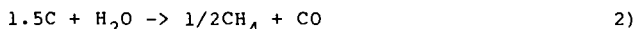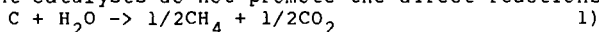
In present gasifiers and catalysts, methane is formed in several ways:

1) devolatilization of coal
2) reaction between CO and H_2O or CO and H_2
3) hydrogasification of coal

The CO, H_2 and CO_2 are formed by the reaction

$$C + H_2O \rightarrow CO + H_2 \qquad 3)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad 4)$$

Methanation of CO (or CO_2) with hydrogen by the reaction

$$CO + 3H_2 \rightarrow CH_4 + H_2O \qquad 5)$$

requires (10) that the CH_4 concentration is lower than:

$$[CH_4] < \frac{[H_2]^3 [CO]}{[H_2O]} K_P \qquad 6)$$

where K_p is the equilibrium constant of reaction 5.
This only occurs when the CH_4 concentration is less than required by global equilibrium.

In the gasification zone the maximum amount of methane that can be generated by gasification is therefore limited by global equilibrium over char (10). There is one exception. At high temperatures the amount of methane generated by devolatilization is larger than is consistent with global equilibrium. This excess methane will react

67

with steam in the reverse reaction (10). However, if this reaction is slow, the methane concentration at the gasifier outlet will be above the global equilibrium.

If SNG is the desired product, then there is an advantage to increasing the direct methane yield in the gasifier. We define here direct methane yield for an SNG process as

$$\text{Direct methane yield} = \frac{CH_4}{CH_4 + \frac{1}{4}(CO + H_2)}$$

where $[CH_4]$, $[CO]$ and $[H_2]$ are the molar fractions of these compounds in the gasifier outlet. Increasing this ratio has two advantages for SNG production.
1) It reduces the cleanup cost of the product gas.
2) It reduces the heat requirements in the gasification zone (or the recycle requirements in the Exxon process). This is only correct if the methane formation occurs in the gasification zone. If the CO formed in a high temperature zone reacts to methane in a low temperature zone, this does not reduce the heat requirements.

The direct yield can be increased by proper utilization of the methane formed in the devolatilization zone (10). This requires a countercurrent scheme such as the one given in Fig. 1, model 2. This scheme can be approximated in a fluid bed by using a two-stage gasifier `such as in model 3. Both countercurrent schemes have the further advantage that the coal is preheated with gasifier effluents. The difference in the thermodynamic constraints between model 2 and 3 is small. We will therefore use model 3 for presenting our results.

The maximum direct methane yield will, therefore, depend also on gasifier design. In a countercurrent or moving bed or two-stage gasifier, the methane from devolatilization has no impact on the global equilibrium. In a one-stage gasifier this methane is generated in the gasification zone and affects the equilibrium.

There are no accurate estimates as to how much methane is formed by devolatilization. This strongly depends on coal, operating conditions, temperature and of partial pressure of steam and hydrogen The best estimates we have are from the BGC slagger and the Dry Ash Lurgi, though in both cases the flow is countercurrent and part of the methane could be formed by methanation in the cool zone just below the devolatilization zone.

Our estimates of the methane formed by devolatilization are taken from ref. 11. There is one more factor that affects direct methane yield. Without a catalyst methanation is slow. Some catalysts promote gasification (reaction 3), but do not promote methanation. We can therefore look at a limiting case in which no methanation occurs in the gasifier.

In Fig. 2 the direct methane yield ratio is plotted for several types of gasifiers operating at global equilibrium with Eastern coal. We choose Eastern coal as our main example since the main need for a catalyst is in the gasification of Eastern caking coals. We give direct methane yield ratio for two pressures (400 and 1000 psia) and for two gasifier models. One, (curve B), is a single stage mixed gasifier. For it we present two limiting cases. In the first we assume global equilibrium in the gasification zone. In the second (curve D) we assume that no methanation occurs in the gasifier, only devolatilization. If the methane yield at global equilibrium is higher than that formed by devolatilization, we assume it to be equal to that formed by devolatilization. If it is lower, we assume that it is equal to global equilibrium. This assumption makes sense at high temperature

since the methane steam reaction is fast without a catalyst.
We also give the results for a two-stage countercurrent gasifier (model III). Here, we also give two cases. One (curve A) in which the methane formation in the gasification zone is at global equilibrium. The other (curve C) where no methane formation occurs in the gasification zone.
Fig. 2 is based on an oxygen steam gasifier operating at equilibrium. Oxygen and steam are fed to the gasifier at $1000^\circ F$. We note that at low temperatures (below $1700^\circ F$) there is very little difference between curve C and D. At still lower temperatures the difference between A and B disappears. The main advantage of prior devolatilization is at higher temperatures. At $1500^\circ F$ the advantage in terms of direct methane yield is significant only for the case where we have a catalyst that promotes methanation in the gasification zone.
We note in Fig. 2 that while increased pressure (Fig. 2b) increases the direct methane yield, the trends are similar in both cases. The main impact of increased pressure is to shift the curves towards higher temperatures.
In Fig. 3 we give the oxygen and steam requirements for SNG production as a function of temperature for a two-stage countercurrent and a one-mixed-stage gasifier. The oxygen and steam requirement are given in the form of the performance parameter proposed in ref. (7) and (8).

$$E_{CH_4} = \frac{H_2O + 4O_2}{CO + H_2 + 4CH_4}$$

which is proportional to the energy requirements to generate the feed for 0.25 mole CH_4. (The 0.25 CH_4 was chosen to make the parameter comparable to the performance parameter used for syngas and fuel gas, see later).
This parameter is an approximate performance parameter which gives different weight to the oxygen and steam requirements in the feed. This weighting factor is based on energy requirement of the feed and correlates quite well with total cost of the feed preparation. Oxygen use also involves another penalty. If its use is more than required by the stoichiometry (8,13), it reduces the cold gas efficiency. To evaluate this we need a complete heat balance of the gasifier. However, simplified performance criteria such as given here, give a reasonable picture of the impact of process parameters on cost and thermal efficiency.
In Fig. 3 we also give actual results for different gasifiers for Eastern coal. None of these is really commercial, but the data in either for a semi-commercial operation (Dry Ash Lurgi, BGC slagger, Texaco), or a large pilot plant (Shell, Westinghouse). We also give the performance of the Exxon process in an equivalent form. The Exxon gasifier does not use oxygen. It reduces the heat of reaction required by cryogenically separating the CO and H_2 from the methane and recycling them to the gasifier. The remaining small heat of reaction is supplied by superheating the recycle stream to $1500^\circ F$ by burning part of the product gas. We try to present this gasifier here in an equivalent form by using an equivalent amount of oxygen. This is obtained by computing the energy used by the cryogenic separation process per mole net methane produced and converting it to oxygen by computing the number of moles of oxygen that could be produced by the same energy. This is reasonable as the cost of an oxygen plant and of the cryogenic separator are quite similar if based on the same energy consumption.
We note that a process operating with oxygen at $1500^\circ F$ close to

69

equilibrium would have an advantage in terms of energy expanded over the Exxon process as proposed.

Figs. 2, 3 and 4 give us a good picture of the potential value of a catalyst that operates at low temperatures. At high temperatures such as in a slagger, it would not affect steam and oxygen consumption. But at low temperatures such as $1400°-1500°F$ its effect would be very beneficial. However, in this case it is essential that the catalyst promotes the methanation reaction.

A two-stage scheme based on such a catalyst at $1500°F$ would be competitive in terms of efficiency with the Exxon gasifier operating at $1300°F$. Its overall thermal efficiency would be slightly better or equal and investment cost would be lower especially if the higher temperature leads to faster reactions and lower residence times.

At $1400°-1500°F$ there is very little chance of ash agglomeration. The main problem would be the agglomeration of caking coals. Pretreatment with a catalyst seems to prevent this phenomenon. Another way out is use of a high velocity mixing zone into which the fresh coal is introduced.

Introduction of fresh oxygen can also cause a locally excessive temperature that would lead to agglomeration. One way of minimizing this is to introduce the oxygen together with the steam and some recycle gas (or coal fines). This would raise steam temperature in the feed. By proper design of the steam nozzles and the mixing zone, this heat would be easier to dissipate than the heat generated by direct combr?r?r?rustion of oxygen inside the gasifier.

?r   There is therefore a strong incentive to look for cheap catalysts?r operating at $1400°F$ to $1500°F$ provided they not only acceler?r?r?rate the gasification reaction but also the methanation reaction. If they promote gasification only, we really deal with a case identical to fuel or syngas production which will be discussed in the next section.

One might even consider using a combination of two catalysts as it is not clear that a cheap efficient gasification catalyst operating at $1500°F$ will also promote methanation. Iron is a good methanation catalyst but loses its activity in the presence of sulphur. Sulphur resistant methanation catalysts are known but are expensive.

Regrettably, most studies in catalysis in coal gasification only report the gasification rate and do not measure the effect of the catalyst on methanation.

If such a catalyst would operate at $1100-1200°F$, then one would be able to get a very simple process of supplying the process heat with superheated steam in a one-stage fluid bed. At $1400-1500°F$ the most promising candidate would be a two-stage fluid bed, the upper stage operating around $1200°F$ and the lower stage at $1400-1500°F$. Heat could be supplied either by direct oxygen introduction or by superheating the steam to high temperatures with oxygen and raw product gas.

2)   Syngas and Fuel Production

Syngas production is similar to fuel gas production, with one important difference. In fuel gas production the percentage of methane in the gas is irrelevant. In syngas production there is a premium for methane free syngas.

For some syngas processes such as methanol and Fischer Tropsch, the presence of methane up to a certain amount (10% of syngas) has only a low penalty in the syngas conversion process. On the other hand, there is a severe penalty to operate a gasifier such that the methane formed by devolatilization is destroyed. The difference in cost for syngas from a BGC slagger as compared to a Shell or Texaco gasifier is such that the incremental methane formed in the slagger is very cheap, both in terms of incremental investment and coal use.

We therefore would like to have a gasifier such as the slagger.

Fig. 5 compares the oxygen and steam requirements (reported as $H_2O + 4O_2$) for a unit of syngas. It is just a replot of Fig. 3 as we deal here with the same constraints. We give here methane a reduced value (half of final product), and therefore use as a criterion

$$E_S = \frac{H_2O + 4O_2}{CO + H_2 + 2CH_4}$$

For fuel gas the denominator would change to $CO+0.85H_2+2.83CH_4$ (see ref. 8). But here we are interested in syngas. The overall conclusions for fuel gas would be very similar.

Looking at this ratio for the various cases in Fig. 5, we note again the advantage of a two-stage countercurrent unit. We also note that the optimum is clearly at a high temperature especially if we want to minimize methane at the same thermal efficiency. A catalyst would not change that. All a catalyst would do is to allow operation at lower temperature close to the equilibrium line.

That means we would have to pay a price for operating at lower temperature. This is justified if we need a gasifier for coals not suited for the slagger, or want to handle fines. It may also lead to simpler, more robust gasifiers.

Another goal would be a gasifier for a smaller plant in which simplicity has a high value. The tars found in the slagger make the total system quite complex and less suitable for smaller sized plants.

Here a gasifier operating close to equilibrium at temperatures around 1500-1800°F could have significant advantages. We want the temperature to be as high as possible, close to the limit dictated by agglomeration. However, gasification at these temperatures is slow. This is especially true at high carbon conversion. Gasification rate seems to drop severely as conversion exceeds 70% (9). One way to achieve high conversion is to operate with excess oxygen. Partial combustion of char to CO is fast. One then has to remove the excess heat. One can either operate at very high temperatures in a single stage gasifier (Shell, Koppers Totzek and Texaco) or use excess steam or recycle gas as a coolant (Winkler, Westinghouse). This reduces the thermal efficiency, as can be noted from Figs. 4 and 5.

All present fluid bed gasifiers operate in the partial combustion regime, using large excesses of oxygen and steam as compared to equilibrium requirement. We define this regime of the oxygen-to-converted coal ratio (8). If this exceeds the ratio required to convert all carbon to CO we call the gasifier a partial combustor.

Ref. (8) shows that the critical ratio of O_2 to carbon that distinguishes gasification from partial combustion can be defined for a coal of composition CH_aO_b as

$$R_{crit} = \frac{1 - b}{2}$$

The values of R for an equilibrium gasifier without methane formation in the gasification zone was given in Fig. 4. Values of the Westinghouse pilot plant, as well as other gasifiers, are given in the same plot. We note that while all equilibrium gasifiers have a value of R less than $R_{critical}$ only the countercurrent gasifiers achieve such low value and in that sense they are at present the only true gasifiers. Cheap catalysts could allow fluid beds to operate in the same regime and thereby increase their efficiency.

Here, the only catalyst property that counts is promotion of reaction (3) at high coal conversion and temperatures of about 1600°F. Several cheap catalysts tested seem to have the property and merit further investigation.

71

3) Devolatilization

One potential area of catalysis that has been completely neglected is the direct reaction of coal with H_2 and steam. When coal devolatilizes primary pyrolysis products are formed (1,12,13,14), which then either decompose into char and gases or react with steam or hydrogen. Sometimes this is called active char, but we really deal with a reaction of pyrolysis intermediates with steam (or hydrogen). This reaction can be promoted by high temperatures and high steam or hydrogen pressure. This involves other penalties. An attractive alternative would be a cheap catalyst that promotes the reaction of pyrolysis products with steam. To be really attractive this catalyst should preferably also promote the decomposition of tars and phenols and should operate at moderate pressures (400 psi) and low temperatures (less than $1400^{\circ}F$).

Shinnar et al. (10) discuss thermodynamic reasons why direct reaction of coal with steam is not likely. It is much more likely to involve an irreversible intermediate step, which would lead to the overall reaction

coal + steam (or hydrogen) -> products + char

The amount of char could be quite small (less than 40%). Study of such reaction in the presence of catalysts at reasonable temperatures and pressures could be of significant value. Another item is the decomposition of tars and phenols found directly in the devolatilization stage, at reasonably low temperatures ($1100-1200^{\circ}F$). Here there are a range of catalysts that could have this effect. The problem is that such catalysts must be effective in reasonably small amounts. Otherwise, the ash removal problem becomes more difficult.

4) Gas cleanup

Devolatilization of coal leads, in addition, to methane, CO and H_2, also to tars and phenols. In a two-stage fluid bed it would be desirable to decompose them in the devolatilization zone, which should be possible and could be one of the main advantages of fluid bed gasifiers. However, in a slagger this is impossible and it would be very desirable if we had a catalyst which could decompose these tars and oxygenate with low excess of steam, which is probably very hard to achieve. However, the gas in a Dry Ash Lurgi used for Western coals contains almost 50% excess steam. A catalyst that decomposes all phenols and tars would make gas cleanup and waste water removal simpler and cheaper for such a gasifier and could have significant value if Dry Ash Lurgi gasifiers ever become more widely used.

Summary and Conclusion

Several key areas have been identified in which proper, cheap disposable catalysts could have significant impact on coal gasification processes.

For SNG production it would be desirable to find a cheaper throwaway catalyst operating at low temperatures, preferably below $1200^{\circ}F$. As such a catalyst is not in sight, one could also achieve significant advantages with a catalyst operating at $1400-1500^{\circ}F$ provided the catalyst (or mixture of catalysts) promotes both gasification and methanation of CO. A gasifier design that could utilize such a catalyst in an optimal way is described.

A catalyst that would promote direct formation of methane (without CO and H_2 as intermediate) would be desirable at high temperatures but no such catalyst is in sight.

For syngas production the advantages are smaller and we require a catalyst that promotes gasification without promoting methanation. Such a catalyst could overcome the inherent disadvantages of fluid beds and allow development of efficient fluid bed gasifiers.

Another area discussed is catalysts that would promote better yields in the devolatilization section by promoting the reactions of

pyrolysis products with steam at low temperatures and pressures, to prevent their polymerization.

Also of potential importance is the catalytic decomposition of tars and oxygenated compounds in the offgases of a Lurgi Dry Ash gasifier.

References

1) Walker, P.L. et al. Kinetics of Coal Pyrolysis and Gasification, DOE Report DE-83012279 (1983).
2) Cabrera, A.L., Heinemann, H., Somooryai, G.A. "Methane Production from Catalyzed Reaction of Graphite and Water Vapor at Low Temperatures (500-600 K)", LBL-12812, 1981.
3) McKee, D.W. "The Catalyzed Gasification Reactions of Carbon," Chemistry and Physics of Carbon, (Ed. P.L. Walker, Jr. and P.A. Thrower), Marcel Dekker Inc., New York), 16, 1(1981).
4) McCoy, L.R. et al., "Investigation of Coal Gasification Catalysis Reaction Mechanism," Quarterly Report, Sept. 1981, Rockwell Science Center, DOE Contract DE-AC21-80MC14592.
5) Kosky, P.G. et al. Coal Gasification Catalysis Mechanism, DOE Report DE-82013824 (1982).
6) Exxon Research & Engineering Co. "Exxon Catalytic Coal Gasification Process", FE-2369-24, 1978.
7) Shinnar, R., Kuo, J.C.W. "Gasifier Study for Mobil Coal to Gasoline Processes", FE-2766-13, 1978.
8) Shinnar, R. Thermodynamic and Process Constraints in Coal Gasification and their Economic Impact. Paper given at METC Symposium on Coal Gasification, Morgantown, November 1983.
9) Johnson, J.L. Adv. Chem. Ser. 1974, No. 131, 145.
10) Shinnar, R., Fortuna, G. and Shapira, D. IEC Process Design and Development 21, 728(1982).
11) Yoon, H., Wei, J., Denn, M.M. "Modelling and Analysis of Moving Bed Coal Gasifiers", Final Report, EPRI AF-590, 1977.
12) Zaharadnik, R.L., Grace, R.J. Adv. Chem. Ser. 1974, No. 131, 127.
13) Gavalas, G.R. Coal Pyrolysis, Elsevier, New York 1982.
14) Solomon, P.R. and Colbet, M.B., 17th International Symposium on Combustion, The Combustion Institute, Pittsburgh 1979.

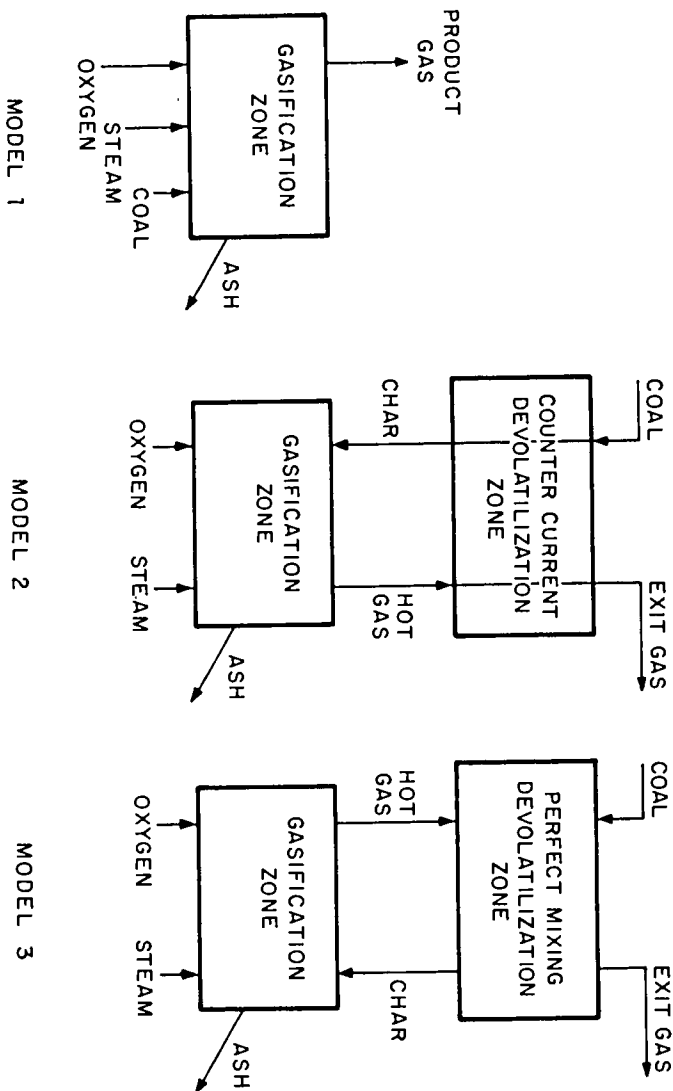# SCHEMATIC REPRESENTATION OF GASIFIERS

MODEL 1

GASIFICATION ZONE

COAL, STEAM, OXYGEN → (inputs)

PRODUCT GAS

ASH

MODEL 2

COAL → COUNTER CURRENT DEVOLATILIZATION ZONE → EXIT GAS

CHAR → GASIFICATION ZONE

OXYGEN, STEAM → GASIFICATION ZONE

HOT GAS

ASH

MODEL 3

COAL → PERFECT MIXING DEVOLATILIZATION ZONE → EXIT GAS

HOT GAS → GASIFICATION ZONE

CHAR

OXYGEN, STEAM → GASIFICATION ZONE

ASH

Fig. 1. Schematic Representation of Gasifier Models.

EASTERN COAL
400 PSI

$$\frac{CH_4}{CH_4 + \frac{1}{4}(CO + H_2)}$$

0.75

○ DRY ASH
✕ SLAGGER
□ WESTINGHOUSE

A
B
C
D

0.00

1200   2100   °F 3000

a: 400 PSI

EASTERN COAL
1000 PSI

$$\frac{CH_4}{CH_4 + \frac{1}{4}(CO + H_2)}$$
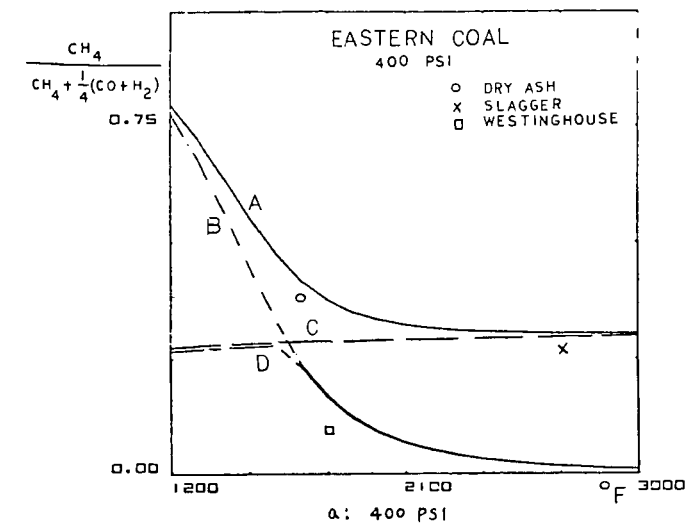
0.75

A
B
C
D

0.00

1200   2100   3000

b: 1000 PSI
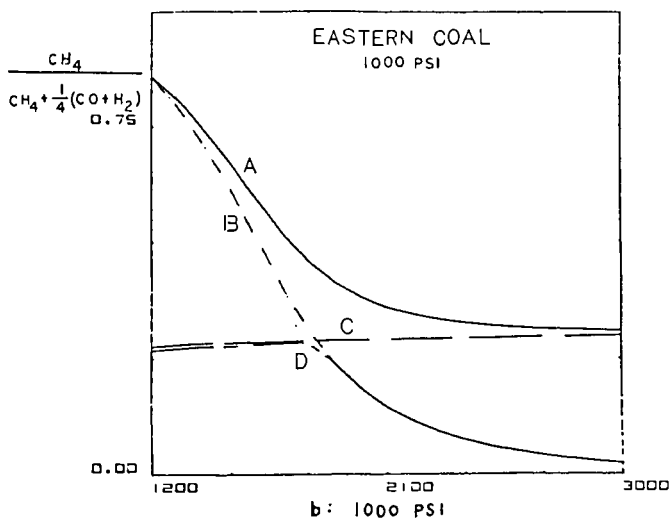
Fig. 2. Direct Methane Yield in a Steam Oxygen-Blown Coal Gasifier at Global Equilibrium.
Effect of pressure, temperature, gasifier design and promotion of the methanation reaction.

A) Two-stage countercurrent gasifier (model III, Fig. 1): Devolatilization in low
   temperature stage (1000°F). Global equilibrium over char in high temperature stage.
   (Temperature shown is temperature of high temperature stage).
B) One-stage mixed gasifier, global equilibrium.
C) Similar to A, but no methane formation in gasifier stage.
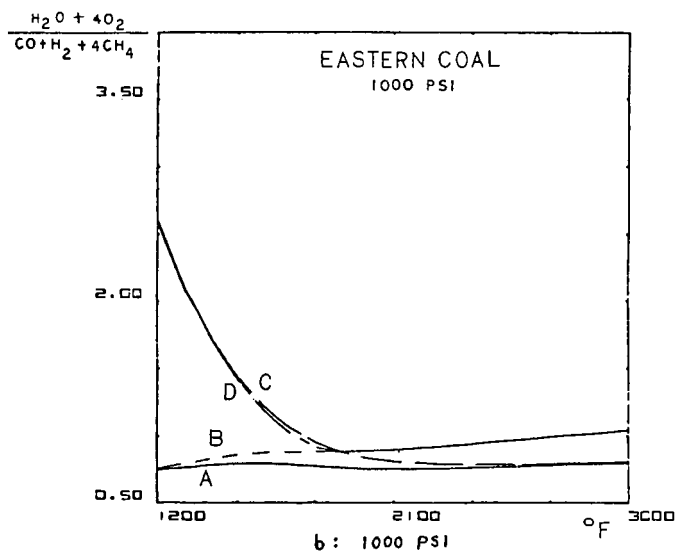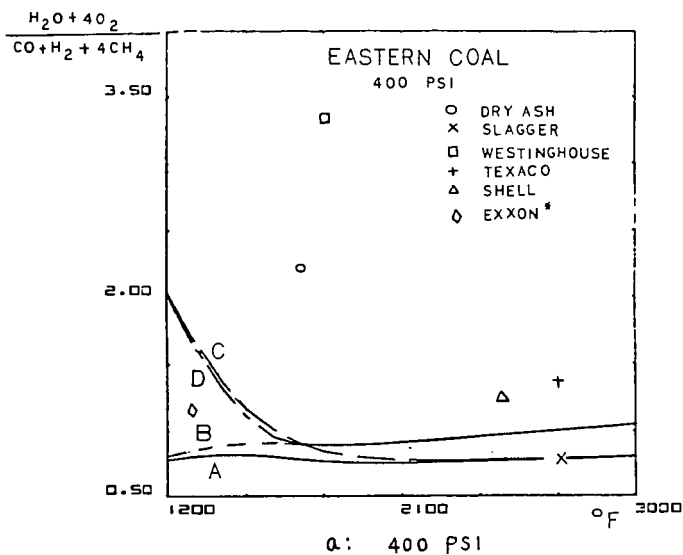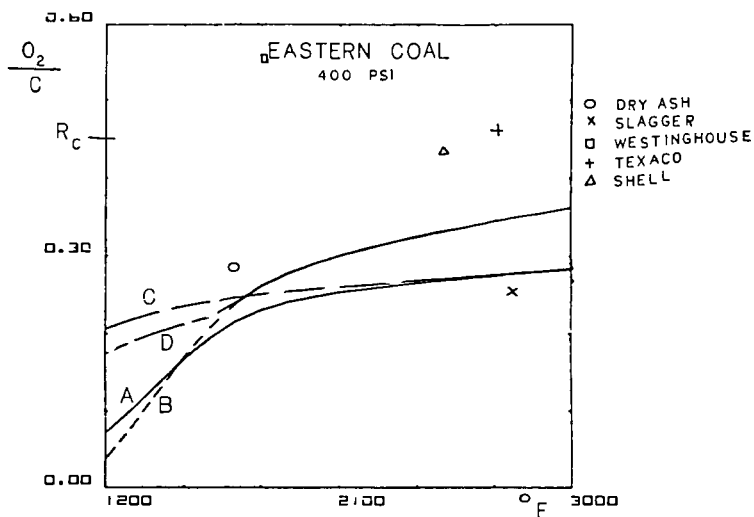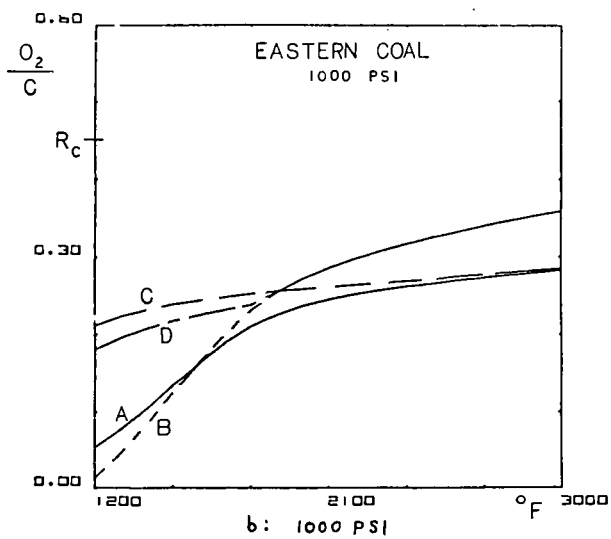D) One-stage mixed gasifier, with devolatilization (see text).

Fig. 3. Oxygen and steam requirements for gasifiers in Figure 1.
For explanation of curves see Figure 2.
*For Exxon gasifier see text for explanation.

a: 400 PSI

b: 1000 PSI

Fig. 4. Oxygen to carbon ratio for gasifiers in Figure 3.

77

$$\frac{H_2O + 4O_2}{CO + H_2 + 2CH_4}$$

EASTERN COAL

400 PSI

O DRY ASH
X SLAGGER
□ WESTINGHOUSE
+ TEXACO
△ SHELL

3.50

2.00

0.50

1200   2100   °F 3000

a: 400 PSI

$$\frac{H_2O + 4O_2}{CO + H_2 + 2CH_4}$$

EASTERN COAL

1000 PSI

3.50

2.00

0.50

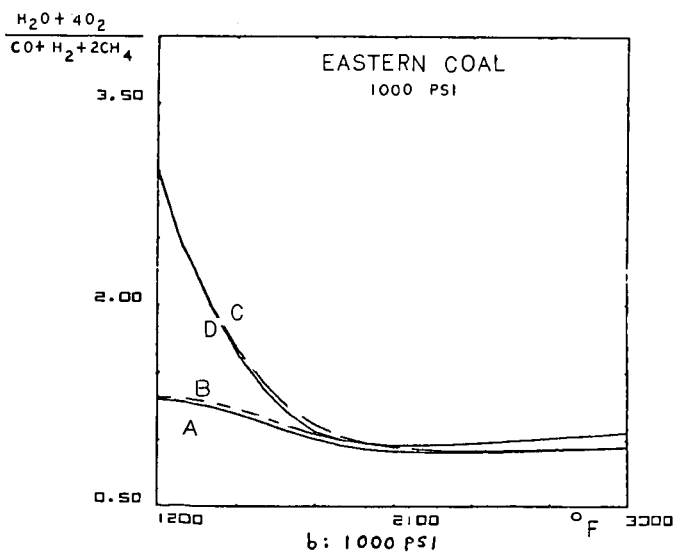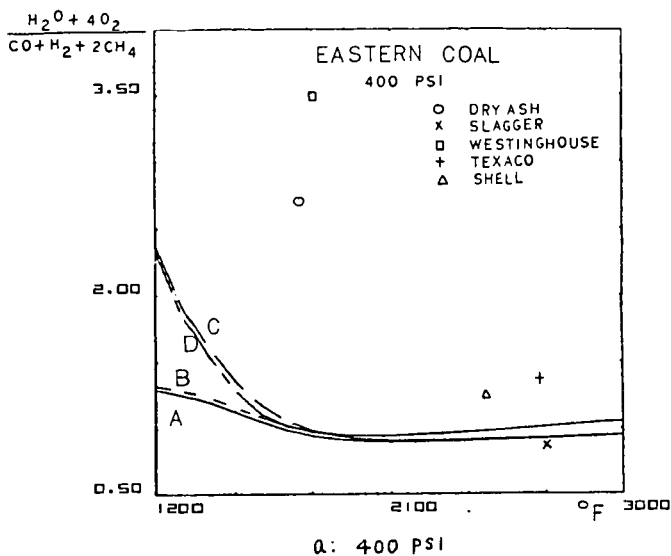1200   2100   °F 3000

b: 1000 PSI

Fig. 5. Oxygen and steam requirements for syngas production (results of Fig. 3 replotted).

78